Non-vacuum Processing of CIGS Solar Cells

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ABSTRACT

This project is directed at developing low-cost, non-vacuum techniques for fabricating photovoltaic (PV) solar cells based on thin-film $CuIn_{1-x}Ga_xSe_2$ (CIGS). Processes for forming both CIGS optical absorber films and metal oxide transparent conducting electrode coatings are being developed. The aim is to accelerate the commercialization of thin-film PV technology by reducing the cost and complexity of fabricating efficient CIGS solar cells. To date CIGS films formed by non-vacuum techniques based on nanoparticle technologies have yielded 11.7% individual cells and 5% monolithic multi-cell submodules.

1. Introduction

Photovoltaic (PV) solar electric technology will be a significant contributor to the Nation's energy supply portfolio when reliable, efficient PV power products are manufactured in large volumes at low costs. A promising pathway to reducing PV costs is the use of thin film technologies in which thin layers of photoactive materials are deposited on inexpensive large-area substrates. One of the most promising thin-film PV technologies is based on $CuIn_{1-x}Ga_xSe_2$ (CIGS). CIGS films and the thin-film electrodes (e.g. ZnO) needed to construct thin-film PV devices are typically deposited by vacuum-based techniques. While vacuum-based techniques can capture a portion of the materials cost savings inherent in thin-film concepts, a promising pathway to reducing capital intensity and functional complexity so as to further reduce costs, increase overall return on investment, and accelerate the transition to large-volume production is the use of non-vacuum techniques for forming PV thin films.

Unisun has pioneered techniques for preparing high-quality PV thin films by non-vacuum techniques, including techniques based on nanoparticle materials [1-4]. Non-vacuum techniques such as spraying and printing are used to deposit thin layers of sub-micron precursor powders, and low-temperature, reactive sintering is used to convert layers into high-quality PV films.

Unisun's work is supported in part by the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) under the auspices of the "Photovoltaic Technologies Beyond the Horizon" program. The *Beyond the Horizon* program is aimed at nurturing basic scientific research directed to identifying and developing non-conventional breakthrough solar electric technologies that will be able to compete with other energy technologies used in the world on a large scale. The basic scientific research supported by the program is directed toward the goal of generating inexpensive electricity from sunlight.

Unisun's work under the *Beyond the Horizon* program is aimed at demonstrating a non-vacuum process for fabricating high-efficiency thin-film CIGS solar cells. The goal is to fabricate efficient thin-film PV devices using non-vacuum processing to deposit high-quality thin films of CIGS alloy optical absorber materials and to deposit coatings of optically-transparent, electrically-conducting metal oxide materials useful for forming solar cell electrodes. The objective of the research is to identify, explore, evaluate, and develop non-conventional solar electric technologies capable of making a breakthrough in the production of low cost electricity from sunlight.

2. Experimental Methods

CIGS films are formed from particulate precursor materials prepared by an aerosol pyrolysis process. Typical CIGS precursor materials are solid sub-micron spheroids containing Cu, In, Ga and O [1]. Layers of precursor particles are deposited by preparing a slurry, paste or ink of precursor material with suitable solvents and dispersing agents, and spraying or printing 2-4 μm thick layers on Mo-coated soda lime glass. Porous precursor layers are converted into dense CIGS films by reactive sintering at 300-600°C.

Solar cells are formed by overcoating p-type CIGS films with n-type transparent conductors and metal grids. A typical processing sequence includes 30-50 nm of a "buffer" material (e.g. CdS, $Zn(S,O,OH)_x$, etc.) and 0.2-2 μm of a conductive semi-transparent metal oxide (e.g. ZnO:Al, ITO, etc.).

Unisun works closely with a range of collaborators. Mo-coated glass is obtained from university and private sector collaborators. CIGS precursor materials, precursor layers and films are processed by Unisun. Some films are processed into cells using CdS buffer layers, ZnO/ITO transparent conductor coatings and Ni/Al grids deposited on Unisun CIGS films by the Institute of Energy Conversion (IEC) by solution deposition, rf sputtering, and e-beam evaporation, respectively. Other CIGS films are processed into cells at Unisun using non-vacuum techniques for depositing non-traditional buffer layers and high-transparency, high-conductance metal oxide films.

3. Experimental Results

Industrial printing techniques can produce planar, well-packed layers of particulate precursor materials. Printed layers are typically more planar and better packed than layers deposited using pneumatic spraying techniques. Average peak-to-valley layer thickness variations are half those typically seen in sprayed layers, and average layer packing density is twice that typically seen in sprayed layers. High-speed printing techniques also provide a 20X increase in precursor layer deposition speed relative to typical pneumatic spraying techniques.

The potential advantages of printing versus spraying are evident from scanning electron microscope data. Scanning electron micrographs (SEM's) of sprayed precursor layers and of sintered CIGS films revealed that baseline as-sprayed layers are non-planar and exhibit low particle packing and that baseline sintered films exhibit moderate void space and layer-derived morphologies [6]. In comparison, printed layers are more planar, and the resulting sintered CIGS films are both denser and more planar [6]. Using well-dispersed slurries, printed layers with average packing densities of 40-60% and average thicknesses of 1-3 μm can be deposited. This compares favorably to sprayed layers with average packing densities of 20-30% and average thicknesses of 3-5 μm (to assure good coverage).

Relative to spraying, high-quality printing requires slurries with higher solids loading (i.e. grams of precursor powder per liter of slurry) and higher viscosities. The functional implementation of printing also requires better slurry stability (e.g. longer-lived particle suspension within the precursor slurry) than do spraying techniques. Batch-to-batch variations in the surface properties of Cu-In-Ga oxide (CIGO) precursor powders can affect the stability of printing slurries. Early printing efforts were compromised by large agglomerates that disrupted the planarity of the printed layer [6].

Organic dispersants can greatly improve the dispersion and suspension of high solids loading slurries. Of the fifteen different organic dispersants tested for dispersion and suspension stability with CIGO precursor powders, three dispersants were found to provide good slurry properties at low dispersant concentrations. The impact of dispersant can be seen in printed layer surface morphology (Figure 1). Printing with dispersants can yield mirror-like printed layers, i.e. very planar layers, in sharp contrast to the most planar layers deposited by spraying.
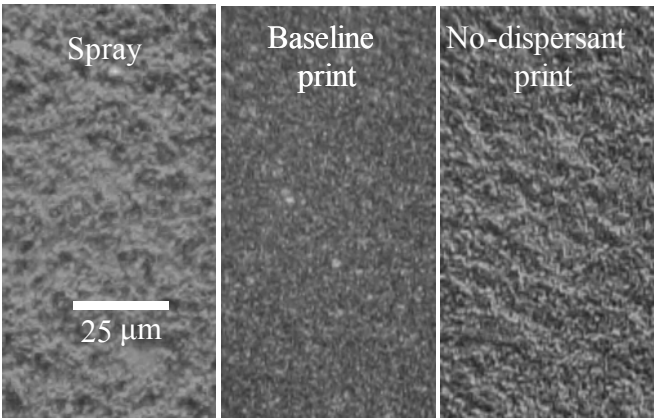

Figure 1: Optical micrographs of sprayed and printed precursor layers

Given the improvements evident in printed layers relative to sprayed layers, significant improvements in cell efficiency were anticipated, but CIGS solar cells fabricated from printed layers of precursor particles yielded sunlight-to-electricity efficiencies at best comparable to cells fabricated using sprayed layers.

Contamination by the additives used to obtain good printing slurries could negatively impact cells fabricated from printed layers. Organic dispersants can leave carbonaceous contamination, though secondary ion mass spectroscopy (SIMS) measurements by Angus Rockett of University of Illinois did not show significant differences in carbon concentrations between films from sprayed and printed layers.

Suspecting other contaminants, alternative dispersants were investigated. Low-residue dispersants yielded printed layer properties similar to those of baseline dispersants, but printed cell efficiencies were still lower than the efficiencies of comparable sprayed cells. Most recently, work has focused on organic-free slurries that can yield reasonably planar printed layers with negligible risk of residual contamination (Fig. 1).

Another potential contributor to low printed cell efficiency is mechanical damage during printing. Small-area printing can be done with non-contact methods (e.g. doctor blades), but large-area, high-speed printing typically has a portion of the printing machinery in contact with the substrate. Off-the-shelf industrial printing equipment resulted in scratches in the Mo electrode layer. Re-engineering of the print head / substrate interface was required to mitigate scratching of the underlying Mo electrode (Figure 2).
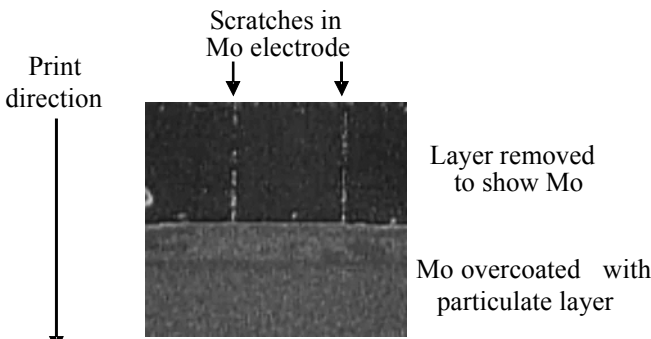

Figure 2: Optical micrographs of printed precursor layers showing Mo scratching by print fixturing.

Thickness control—both run-to-run and spatial uniformity on any one substrate—requires close control of a variety of printing variables, including printing speed, slurry metering and printing hardware set-up. Improvements to off-the-shelf industrial printing equipment improved printed layer repeatability and uniformity from +/- 35% to better than +/- 10%, well within acceptable ranges for compositionally uniform particles.

Layers of Cu-In-Ga oxide particulate precursor materials are converted into CIGS films by a reactive sintering process similar in many respects to metals-to-CIGS selenization / sulfurization processes reported in the literature. Porous layers of precursor particles are heated in an atmosphere containing volatile reactants; metal/oxide precursor materials are converted to the target chalcogenide. Relative to sprayed layers, baseline sintering of printed layers typically yielded cells with lower photovoltages and lower photocurrents, even when care was taken to avoid print-related problems (e.g. slurry dispersant residues, Mo scratches, etc.). Analyses suggested that lower average cell efficiencies were linked to the structure of the printed layers themselves, and the impacts

that layer structure can have on film composition. Relative to sprayed layers, printed layers are more planar and better packed, and thus it is more difficult for volatile sintering reactants to diffuse into the full depth of printed layers. Though x-ray diffraction measurements did not show significant concentrations of residual oxygen, it appeared that printed layers were in effect under sintered.

Two types of more aggressive sintering were explored. In the first set of experiments, more aggressive reactive sintering conditions (e.g. higher temperatures, longer times, higher reactant concentrations, etc.) were used. The aim was to increase the thermodynamic driving forces for diffusing reactants into printed layers and for converting the metal/oxide layers into chalcogenide films. Relative to baseline sintering of printed layers, more-aggressive sintering conditions increased typical photovoltages by 25-35 rel%, but had only a modest impact on photocurrent densities. Unlike cells fabricated from sprayed layers sintered under such conditions, devices fabricated from printed layers did not show selenization of the underlying Mo, suggesting that the printed layers did indeed slow reactant diffusion. The surface morphologies were comparable to printed layers sintered under baseline conditions.

In the second set of experiments, printed layers were pre-annealed prior to introducing selenium and/or sulfur reactants. Relative to baseline sintering of printed layers, pre-anneals coupled with baseline sintering increased typical photovoltages by 15-35 rel% and increased typical photocurrent densities by 65-85 rel%. Optical micrographs of layers subjected to moderate pre-anneals show slightly rougher surfaces than do those of layers subjected only to baseline sintering (Figures 3a, 3b). Optical micrographs of layers subjected to more aggressive pre-anneals show much rougher sintered film surfaces, suggestive of melting and/or dewetting (Figure 3c).
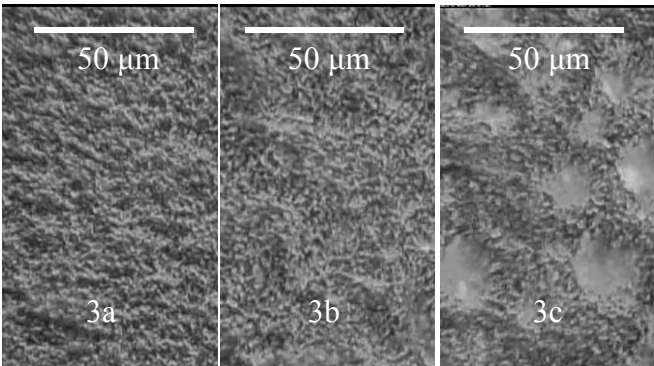
Figure 3: Optical micrographs of CIGS films fabricated using printed layers using (a) baseline sintering, (b) moderate pre-annealing, and (c) aggressive pre-annealing.

Refinements to the early stages of the sintering profile (e.g. time, temperature and reactant concentrations) were successful in increasing apparent CIGS film grain size (Figure 4).
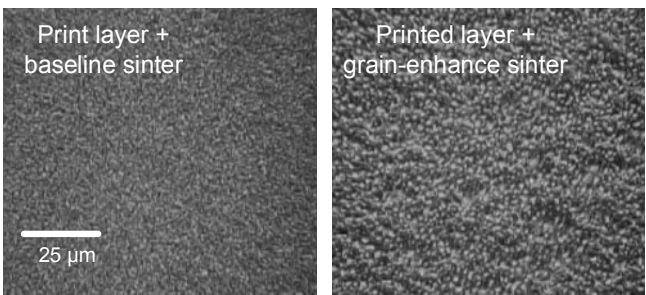

Figure 4: Optical micrographs of CIGS films made from printed layers using baseline and grain-enhancing sintering.

Non-vacuum processes were also used to deposit buffer materials and transparent, conducting metal oxides.

Work on buffer layers focused on developing CdS and Zn-based buffer layers deposition processes suitable for non-vacuum processed CIGS. CdS buffer layers were deposited by typical aqueous solution deposition processes. The CIGS film surface morphology affects the nature of the buffer layers necessary for efficient solar cells. In order to mitigate interfacial shunting that can reduce photovoltage and fill factor, cells prepared using relatively non-planar CIGS films prepared from sprayed nanoparticulate precursor layers require thicker buffer layers than do more-planar vacuum-deposited CIGS films [6].

Work on non-vacuum deposition of transparent conductor coatings focused on nanoparticulate metal oxide materials. Conductive coatings can be formed by depositing layers of nanoparticulate materials, but it is generally difficult to obtain low sheet resistances without high-temperature sintering. Even when using high-conductivity particles, layers of particulate materials generally exhibit high sheet resistances due to poor electrical transport between adjacent particles.

Coatings prepared from spray-deposited layers of ZnO:Al nanoparticles exhibited high coating porosities, rough surface morphologies, low specular optical transparencies, and sheet resistances above 1 MΩ/sq. Spin-coated layers of doped tin oxides were more successful in forming dense, mechanically-hard coatings with good optical transparencies. Single-layer coatings of ITO nanoparticles annealed in air at 170 - 200°C yielded initial sheet resistances as low as 600 ohms per square for a 150 nm thickness on bare glass (Figure 5).
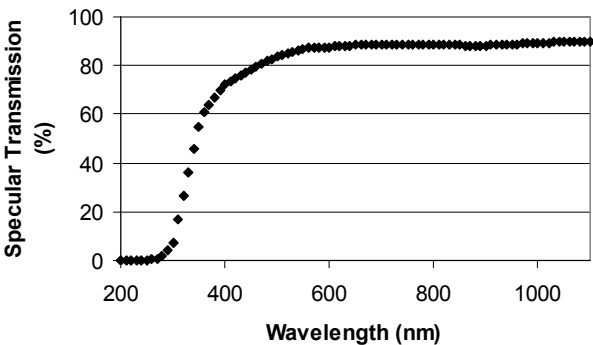

Figure 5 : Specular optical transmission for spin-coated ITO nanoparticulate coating

Aqueous and non-aqueous slurry formulations were explored. Absent organic additives, water-based formulations generally exhibited poor wetting on bare glass. Additions of simple alcohols at low concentrations significantly improved wetting to glass.

Metal oxide coatings were also deposited by non-vacuum, non-particulate means. Tin oxide coatings were deposited by spin-coating, drying, pyrolyzing and recrystallizing layers of organic reactant solutions from Chemat Technologies. Thin, continuous, crack-free, transparent coatings were achieved, but reasonable electrical sheet conductances required air annealing at temperatures above 500°C.

Conducting polymers provide another non-vacuum, non-particle route to low-temperature TC coatings. Sheet resistances below 300 ohms per square have been achieved with 0.3-micron thick coatings processed at room temperature [6]. Optical transmission of these first-generation coatings is lower than optimal over the wavelength range of interest for CIGS; and the organic coatings are mechanically soft, hence would likely require a protective hard top coating (e.g. spin-coated silica).

Solid metal oxide coatings can also be deposited by low-temperature spray pyrolysis methods. ZnO coatings have been deposited using inorganic reactant solutions sprayed in air at 150°C. As with nanoparticulate formulations, aqueous reactant solutions generally exhibit poor wetting on glass at low temperatures. Alcohol additions improve wetting, but alter the deposited film such that a sharp ZnO optical band edge is not evident until after air annealing at 250°C. Wetting of aqueous solutions--hence sprayed film quality--is significantly improved by the pre-deposition of thin (e.g. 50 nm) ZnO films by dip coating. For example, a spray-pyrolyzed ZnO layer deposited at 150°C on to glass previously pre-coated with ZnO by dip coating process using a non-aqueous reactant solution yielded excellent optical characteristics (Figure 6).
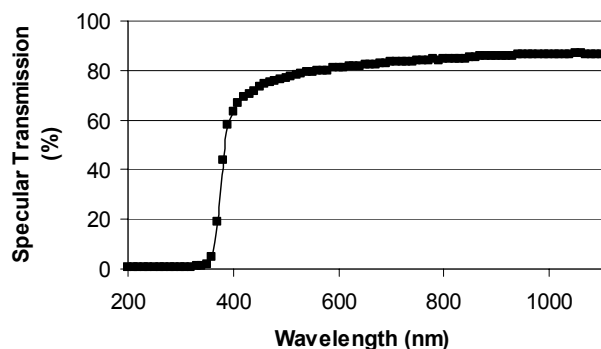

Figure 6: Specular optical transmission for spray-pyrolyzed ZnO on dip-coated ZnO

Work is now focused on hybrid coatings comprising particulate conductors embedded in solid conductive matrices. Numerical modeling suggests that comparatively low conductance of a intercalating matrix will be sufficient to yield much improved particle-based TC coating conductances.

CIGS solar cells fabricated using first-generation non-vacuum transparent conductor coatings showed modest sunlight-to-electricity efficiencies. The primary limitations were sheet resistance and photocollection losses in the case of high-sheet resistance inorganic coatings and shunting in the case of bare, low-sheet resistance organic coatings. Improved cell gridding techniques are being evaluated to mitigate shunting.

5. Conclusions

This project aims to demonstrate the feasibility of using particulate precursor materials in a simple, easily scalable, non-vacuum process for depositing CIGS films for large-area, low-cost PV modules.

High-speed, high-efficiency industrial printing techniques have been shown suitable for depositing nanoparticulate precursor layers for forming high-quality CIGS films. Advances in layer-to-film reactive sintering techniques have produced compositionally-uniform, particle-derived CIGS absorber films with large grains. Non-vacuum processes have been used to deposit transmissive conducting coatings suitable for use as transparent electrodes in thin-film solar cells.

Non-vacuum processes promise to halve the cost of the PV films in a thin-film solar module, to increase the return on investment for thin-film PV, and to significantly accelerate the large-scale commercialization of CIGS PV technology.

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